746. *The Preparation and Complex-forming Properties of One Tritertiary and One Tetratertiary Phosphine.*

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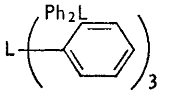
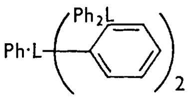
The preparation of tris-(*o*-diphenylphosphinophenyl)phosphine and bis-(*o*-diphenylphosphinophenyl)phenylphosphine is described. Complexes of the former with palladium(II) and platinum(II) are five-co-ordinate with trigonal bipyramidal co-ordination, but those of ruthenium(II) and osmium(II) are six-co-ordinate. Complexes of the latter ligand with platinum(II) and palladium(II) are four-co-ordinate in solid state and in solution.

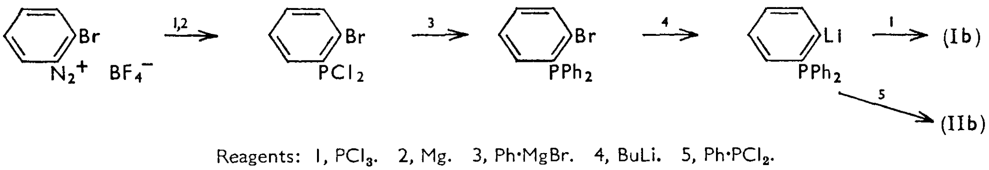
The unusual complexes[1-3] produced by tris-(*o*-diphenylarsinophenyl)arsine (Ia) and bis-(*o*-diphenylarsinophenyl)phenylarsine (IIa) prompted us to prepare their phosphorus analogues (Ib) and (IIb), respectively. These ligands were obtained by the methods indicated in the scheme. They form white crystals, stable in air, moderately soluble in aromatic hydrocarbons and ethanol, and very soluble in tetrahydrofuran.

(Ia: L = As) (QAS)
(Ib: L = P) (QP)





(IIa: L = As) (TAS)
(IIb: L = P) (TP)



Reagents: 1, PCl_3. 2, Mg. 3, Ph·MgBr. 4, BuLi. 5, $Ph{\cdot}PCl_2$.

The complexes with the phosphorus ligands (see Table 1) were obtained in conditions similar to those used for their arsenic analogues,[1-3] but were obtained more readily.

The starting material for the preparation of the osmium complexes with ligands (Ia

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[1] Brewster, Savage, and Venanzi, *J.*, 1961, 3699

[2] Hartley and Venanzi, *J.*, 1962, 182.

[3] Savage and Venanzi, *J.*, 1962, 1548.

TABLE 1.

Colour, decomposition point, molar conductance, and magnetic susceptibility of complexes of the ligands (Ia and b) and (IIa and b) with palladium(II), platinum(II), ruthenium(II), and osmium(II).

Complex	Colour	Decomp. pt.	Λ_M * (mhos)	$10^6\chi_M$
$[PdCl(QP)]Cl$	Dark red	307—309°	21·8	−15
$[PdCl(QP)][BPh_4]$	Red	248—251	18·6	—
$[PdI(QP)]I$	Red-purple	303—308	20·6	+25
$[PdI(QP)][BPh_4]$	Red-purple	257—260	18·7	—
$[PtCl(QP)]Cl$	Orange-yellow	352—356	24·6	+25
$[PtCl(QP)][BPh_4]$	Yellow	309—312	18·6	—
$[PtI(QP)]I$	Orange	362—365	24·2	—
$[PtI(QP)][BPh_4]$	Orange-yellow	311—314	19·5	—
$[RuCl_2(QP)]$	Pale yellow	>380	0	+120
$[OsCl_2(QP)]$	Pale yellow	>380	0	—
$[OsCl_2(QAS)]$	Pale yellow	>380	0	+80
$[PdCl_2(QAS)]Cl_2$	Yellow	306—310	44·2	+25
$[PtCl_2(QAS)]Cl_2$	Pale yellow	324—328	45·1	+35
$[PdI(TP)]I$	Yellow-orange	322—324	24·1	—
$[PdI(TP)](ClO_4)$	Yellow-orange	336—339	27·4	—
$[PtI(TP)]I$	Yellow	358—360	25·2	—
$[PtI(TP)](ClO_4)$	Yellow	364—366	28·4	—
$[PdBr_2(TAS)]$	Orange-red	331—334	11·6	+15

* For 10^{-3}M-nitrobenzene solutions at 19°.

and b) was the salt $K_2[Os(OH)(NO_2)_4(NO)]$,[4] described by Wintrebert [5] and formulated by him as $K_2[Os(NO_2)_5]$.

The similarity in physical properties between the complexes with ligands (Ia and b) leads us to assign trigonal-bipyramidal co-ordination to the platinum(II) * and palladium(II) complexes,[1,3] and a six-co-ordinate structure to the ruthenium(II) and osmium(II) ones.[2] The visible and ultraviolet spectra of the complexes are given in Table 2. The low-frequency absorption bands of the phosphorus complexes, as expected,[7] occur at higher frequencies than those of the arsine complexes. The shifts are much larger in the d^6- than in the d^8-complexes (see Figs.), a fact which can be associated with the smaller energy-level splittings for trigonal-bipyramidal complexes.[8]

The ruthenium(II) and osmium(II) complexes show a residual paramagnetism which, at least in the case of $[Ru(CNS)_2(QAS)]$, is temperature-independent.

As shown in a previous paper,[2] potentiometric titration of $[PtCl(QAS)](ClO_4)$ with chlorine indicates its smooth oxidation to the corresponding platinum(IV) derivative. However, when such titration was attempted on the salt $[PdCl(QAS)](ClO_4)$, it was observed that the measured e.m.f. varied erratically as chlorine was added. Oxidation experiments, when carried out on a preparative scale, with $[MCl(QAS)]Cl$ (M = Pd or Pt) and chlorine gave a six-co-ordinate complex $[MCl_2(QAS)]Cl_2$ (see Table 1). In the preparation of the palladium(IV) complex, however, a large excess of chlorine was necessary to afford the desired product, indicating that the difference in stability of the M(II)/M(IV) couple (M = Pd or Pt) is maintained in our complexes.

The complexes of the tritertiary phosphine (IIb) with palladium(II) and platinum(II) are 1 : 1 electrolytes in nitrobenzene (see Table 1) and are presumably four-co-ordinate. By contrast, the complex $[PdI_2(TAS)]$ is only partially dissociated in this solvent,[3] showing preferential five-co-ordination. This observation is in good agreement with the

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* The complex $[PtI(QAS)][BPh_4]$ has trigonal-bipyramidal structure,[1] and not square-pyramidal structure as stated by Barclay *et al.*[6]

[4] Irving, Lewis, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.

[5] Wintrebert, *Ann. Chim. Phys.*, 1903, **28**, 15.

[6] Barclay, Nyholm, and Parish, *J.*, 1961, 4433.

[7] Chatt, Gamlen, and Orgel, *J.*, 1959, 1047.

[8] Ballhausen and Jørgensen, *Kgl. danske Videnskab. Selskab, Mat.-fys. Medd.*, 1954, **29**, no. 4.

TABLE 2.

Wavelength of absorption ($\lambda_{max.}$), energy of absorption ($E_{max.}$), and molar extinction coefficients (ε) of complexes of palladium(II), platinum(II), ruthenium(II), and osmium(II) with tridentate and tetradentate phosphorus and arsenic ligands.

	Solution †			Solid		
Complex	$\lambda_{max.}$ (mμ)	$E_{max.}$ (kK)	ε (l. mole^{-1} cm.$^{-1}$)	$\lambda_{max.}$ (mμ)	$E_{max.}$ (kK)	" D "
$[PdCl(QP)]Cl$	233	43·00	59,800			
	264	37·95	sh			
	310	32·30	sh	365	27·4	sh
	454	22·05	6650	459	21·8	* 1·65
	485	20·60	sh	500	20·0	
$[PdCl(QP)][BPh_4]$	232	43·10	81,050		Not recorded	
	263	38·00	sh			
	310	32·30	sh			
	455	22·00	7580			
	483	20·70	sh			
$[PdI(QP)]I$	233	42·90	73,800		Not recorded	
	258	38·80	sh			
	373	26·80	6850			
	515	19·40	6220			
$[PdI(QP)][BPh_4]$	232	43·10	90,000		Not recorded	
	258	38·80	48,100			
	373	26·80	8750			
	515	19·40	7000			
$[PtCl(QP)]Cl$	275	36·40	20,200			
	325	30·80	sh			
	391	25·95	5500	385	26·0	* 1·63
	424	23·60	sh	456	22·0	
$[PtCl(QP)][BPh_4]$	229	43·60	90,000		Not recorded	
	266	37·60	sh			
	392	25·50	5950			
	439	22·80	sh			
$[PtI(QP)]I$	230	43·50	74,500		Not recorded	
	314	31·80	sh			
	439	22·80	4610			
	450	22·20	sh			
$[PtI(QP)][BPh_4]$	229	43·70	87,500		Not recorded	
	309	32·40	sh			
	435	23·00	4950			
	459	21·80	sh			
$[RuCl_2(QP)]$	231	43·30	42,900		Not recorded	
	239	41·80	sh			
	403	24·80	5150			
$[OsCl_2(QAS)]$	228	43·90	61,000		Not recorded	
	290	34·50	sh			
	325	30·80	8000			
$[OsCl_2(QP)]$	229	43·70	54,200		Not recorded	
	302	33·10	8200			
$[PdCl_2(QAS)]Cl_2$	229	43·60	55,220		Not recorded	
	262	38·20	sh			
	379	26·40	3380			
$[PtCl_2(QAS)]Cl_2$	264	37·90	sh	357	28·00	sh
	360	27·80	7400			
$[PdI(TP)]I$	233	43·00	60,600			
	315	31·70	10,600			
	379	26·40	3120	380	26·30	* 1·66
	417	24·00	sh	420	23,80	
$[PdI(TP)](ClO_4)$	233	43·00	60,700		Not recorded	
	253	39·50	sh			
	314	31·80	10,790			
	380	26·30	4000			
	417	24·00	sh			
$[PtI(TP)]I$	231	43·20	80,000			
	326	30·70	5250	340	29·40	1·43
$[PtI(TP)](ClO_4)$	231	43·20	60,800			
	260	38·50	sh			
	325	30·80	5450	339	29·50	1·20

TABLE 2. (*Continued.*)

	Solution †			Solid		
Complex	$\lambda_{max.}$ (mμ)	$E_{max.}$ (kK)	ε (l. mole^{-1} cm.$^{-1}$)	$\lambda_{max.}$ (mμ)	$E_{max.}$ (kK)	" D "
$[PdBr_2(TAS)]$	231	43·20	58,200			
	282	35·40	27,400			
	444	22·50	4920	446	22·40	1·61
$[PdBr_2(TAS)]$ ‡	299	33·40	23,100			
	389	25·70	3200			

* Broad band. † In dichloromethane. sh = shoulder. ‡ In ethanol solution; not recorded above 35,000 cm.$^{-1}$.

hypothesis that lower co-ordination numbers will be found when the metal ion is co-ordinated to π-bonding ligands.[3] Since phosphorus is believed to form stronger π-bonds than arsenic,[9] the tritertiary phosphine (IIb) should show less tendency to form five-co-ordinate complexes than the corresponding tritertiary arsine (IIa). It must be pointed out, however, that Barclay *et al.*[6] have suggested that the tendency to form five-co-ordinate d^8 complexes increases as (i) the formal charge on the metal atom decreases, (ii) the effective nuclear charge on the metal atom decreases, and (iii) the polarisability of the anion increases. If it is assumed that the effect of increasing polarisability on co-ordination numbers applies to uncharged ligands as well as to anionic ones, our results could be explained without invoking π-bonding. In our complexes, however, effect (iii) does not appear to operate: the molar conductances of complexes $[PdBr_2(TAS)]$ and $[PdI_2(TAS)]$

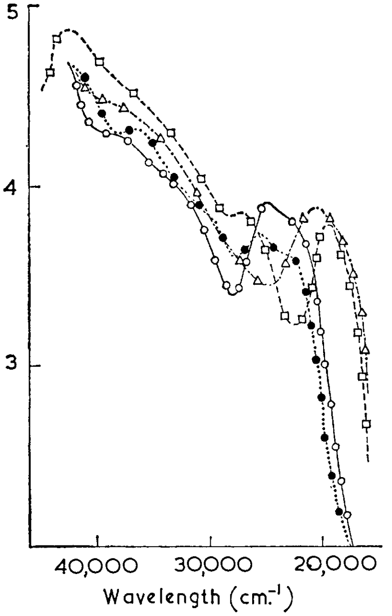

FIG. 1. Visible and ultraviolet spectra of complexes of ligands (Ia and b) with palladium(II) and platinum(II).

Δ-·-·Δ $[PdCl(QP)]Cl$;
□ - - - □ $[PdCl(QAS)]Cl$;
● · · · · ● $[PtCl(QP)]Cl$;
○——○ $[PtCl(QAS)]Cl$.

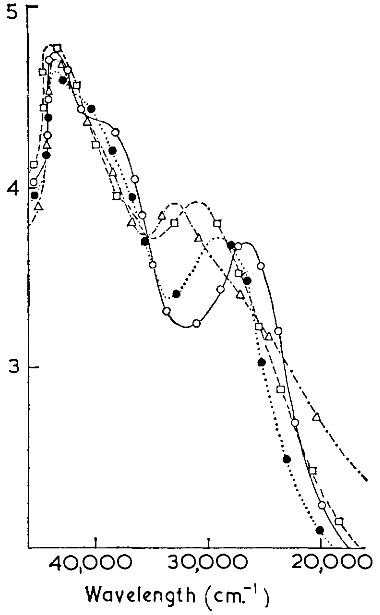

FIG. 2. Visible and ultraviolet spectra of complexes of ligands (Ia and b) with ruthenium(II) and osmium(II).

● · · · · ● $[RuCl_2(QP)]$;
○——○ $[RuCl_2(QAS)]$;
Δ-·-·Δ $[OsCl_2(QP)]$;
□ - - - □ $[OsCl_2(QAS)]$.

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[9] Chatt and Wilkins, *J.*, 1952, 4300.

in nitrobenzene are practically identical over the concentration range 1—3 × 10^{-3}M and differ only slightly at higher dilutions (see Experimental section).

EXPERIMENTAL

o-*Bromophenyldichlorophosphine* was prepared by the method of Quin and Humphrey,[10] from *o*-bromophenyldiazonium fluoroborate (125 g.) in 21% yield. It had b. p. 90—93°/0·9 mm. (Found: P, 11·8. $C_6H_4BrCl_2P$ requires P, 12·0%).

o-*Bromophenyldiphenylphosphine.*—*o*-Bromophenyldichlorophosphine (24 g.) in dry ether (50 c.c.) was treated with phenylmagnesium bromide (10% excess) in ether (150 c.c.). The product, on recrystallisation from ethanol, gave prisms, m. p. 112—113° (36%) (Hart [11] gives m. p. 114°).

Tris-(o-*diphenylphosphinophenyl*)*phosphine* (Ib).—*o*-Bromophenyldiphenylphosphine (11·6 g.) in ether (50 c.c.) was treated with 0·985N-ethereal n-butyl-lithium (35 c.c.), and the lithium derivative formed was treated with phosphorus trichloride (1 c.c.) in ether (50 c.c.). The solid residue obtained on hydrolysis was filtered off (7 g.) and recrystallised from dimethylformamide as prisms, m. p. 221—223°, of *monosolvate* (Found: C, 77·1; H, 5·6; N, 1·2; P, 13·8. $C_{57}H_{49}NOP_4$ requires C, 77·1; H, 5·6; N, 1·4; P, 13·95%).

Bis-(o-*diphenylphosphinophenyl*)*phenylphosphine* (IIb).—Dichlorophenylphosphine (2·3 c.c.) in ether (50 c.c.) was added to a solution of *o*-lithiophenyldiphenylphosphine (from 10·7 g. of *o*-bromophenyldiphenylphosphine). The product (2·3 g.) recrystallised from dimethylformamide as prisms, m. p. 226—228°, of *monosolvate* (Found: N, 1·8; P, 13·45. $C_{45}H_{40}NOP_3$ requires N, 2·0; P, 13·2%).

Tris-(o-*diphenylphosphinophenyl*)*phosphine Complexes.*—[PtCl(QP)]Cl. Sodium chloroplatinite tetrahydrate (0·23 g.) in ethanol (20 c.c.) was added to a boiling suspension of the ligand (0·46 g.) in ethanol (20 c.c.). After refluxing for 3 hr. the solution was evaporated *in vacuo*, leaving the *product* which recrystallised (0·35 g.) from chlorobenzene (Found: Pt, 17·9; P, 11·25. $C_{54}H_{42}Cl_2P_4Pt$ requires Pt, 18·05; P, 11·45%).

[PtCl(QP)][BPh_4]. The chloro-chloride above (0·08 g.) in ethanol was treated with a slight excess of sodium tetraphenylborate, the precipitated *complex* was filtered off, dissolved in dichloromethane, and reprecipitated with ethanol (Found: Pt, 14·4; P, 9·1. $C_{78}H_{62}BClP_4Pt$ requires Pt, 14·3; P, 9·1%).

[PtI(QP)]I. The chloro-chloride (0·125 g.) was refluxed in ethanol (30 c.c.) with sodium iodide (0·06 g.) for 4 hr. The orange solution was filtered from the precipitated sodium chloride and evaporated *in vacuo* to leave the *complex* (0·129 g.) which recrystallised from nitromethane (Found: Pt, 15·2; P, 9·9. $C_{54}H_{42}I_2P_4Pt$ requires Pt, 15·4; P, 9·8%).

[PtI(QP)][BPh_4]. This *salt* was prepared and purified as was its chloro-analogue (Found: Pt, 13·2; P, 8·5. $C_{78}H_{62}BIP_4Pt$ requires Pt, 13·4; P, 8·5%).

[Pd(QP)Cl]Cl. This *chloride* was prepared similarly to its platinum analogue and recrystallised from nitromethane (Found: Pd, 10·65; P, 12·4. $C_{54}H_{42}Cl_2P_4Pd$ requires Pd, 10·75; P, 12·5%).

The following *complexes* were prepared and purified similarly to their platinum analogues: [PdI(QP)]I (Found: Pd, 8·95; P, 10·5. $C_{54}H_{42}I_2P_4Pt$ requires Pd, 9·05; P, 10·5%). [PdCl(QP)][BPh_4] (Found: Pd, 8·2; P, 9·6. $C_{78}H_{62}BClP_4Pd$ requires Pd, 8·35; P, 9·7%). [PdI(QP)][BPh_4] (Found: Pd, 7·8; P, 9·15. $C_{78}H_{62}BIP_4Pd$ requires Pd, 7·8; P, 9·05%).

The complex [$RuCl_2$(QP)]. Dry hydrogen chloride was passed through a solution of the salt $K_2[Ru(OH)(NO_2)_4(NO)]$ (0·22 g.) in tetrahydrofurfuryl alcohol (20 c.c.) at 100° for 30 min. The ligand (0·45 g.) was added to the violet suspension of the chloro-complex $K_2[RuCl_5(NO)]$ formed,[2] the mixture refluxed for 3 hr., and the resulting brown solution evaporated at the oil-pump. Tetrahydrofuran (25 c.c.) was added, and the *complex* (0·3 g.) filtered off and purified by repeated precipitation from methylene chloride solution by carbon tetrachloride (Found: Ru, 10·9; P, 12·4. $C_{54}H_{42}Cl_2P_4Ru$ requires Ru, 10·85; P, 12·55%).

The complex [$OsCl_2$(QP)]. Dry hydrogen chloride was passed through a suspension of the salt $K_2[Os(OH)(NO_2)_4(NO)]$[4] in absolute alcohol. The resulting yellow-brown solution was filtered from potassium chloride and evaporated to dryness, leaving a yellow-brown solid

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[10] Quin and Humphrey, *J. Amer. Chem. Soc.*, 1961, **83**, 4124.
[11] Hart, *J.*, 1960, 3324.

which was assumed to be the substance [$OsCl_3(NO)$]. This (0·16 g.) was refluxed in tetrahydrofurfuryl alcohol (20 c.c.) with the ligand (Ib) (0·4 g.) for 6 hr. The *product* was isolated and purified as described for the analogous ruthenium complex (Found: Os, 17·6; P, 11·4. $C_{54}H_{42}Cl_2OsP_4$ requires Os, 17·65; P, 11·5%).

Bis-(o*-diphenylphosphinophenyl*)*phenylphosphine Complexes.*—[PdI(TP)]I. Palladous iodide (0·25 g.), the ligand (IIb) (0·4 g.), and sodium iodide (0·05 g.) were refluxed for 12 hr. in ethanol (50 c.c.) and chloroform (10 c.c.). The orange solution was filtered and evaporated *in vacuo*, leaving the *complex* (0·36 g.) which was repeatedly precipitated from methylene chloride solution by light petroleum (Found: Pd, 10·7; P, 9·2. $C_{42}H_{33}I_2P_3Pd$ requires Pd, 10·75 P, 9·35%).

[PdI(TP)](ClO_4). The above iodo-iodide (0·1 g.) in ethanol (30 c.c.) was treated with sodium perchlorate (0·02 g.) and left overnight. The precipitated yellow-orange *perchlorate* (0·07 g.) was filtered off and purified by precipitation from dichloromethane solution by ethanol (Found: Pd, 11·1; P, 9·7. $C_{42}H_{33}ClIO_4P_3Pd$ requires Pd, 11·05; P, 9·65%).

[PtI(TP)]I. Sodium chloroplatinite tetrahydrate (0·35 g.) in ethanol (10 c.c.) was added to a solution of sodium iodide (0·4 g.) in ethanol (8 c.c.) and after 2 hr. the precipitated sodium chloride was filtered off. The filtrate was refluxed with the ligand (IIb) (0·44 g.) for 3 hr. The *product* (0·52 g.) was filtered off, washed with tetrahydrofuran, and recrystallised from nitromethane (Found: Pt, 17·9; P, 8·55. $C_{42}H_{33}I_2P_3Pt$ requires Pt, 18·05; P, 8·6%).

[PtI(TP)](ClO_4). This *salt* was prepared similarly to its palladium analogue (Found: Pt, 18·65; P, 8·7. $C_{42}H_{33}ClIO_4P_3Pt$ requires Pt, 18·55; P, 8·8%).

Dibromobis-(o*-diphenylarsinophenyl*)*phenylarsinepalladium*(II), [$PdBr_2$(TAS)].—Sodium bromopalladite (0·2 g.) in ethanol (20 c.c.) was refluxed with the ligand (IIa) (0·3 g.) for 2 hr. The *complex* crystallised from the orange-yellow solution overnight (0·245 g.) and recrystallised from ethanol (Found: Pd, 10·3; As, 21·6. $C_{42}H_{33}As_3Br_2Pd$ requires Pd, 10·4; As, 21·8%).

Tris-(o*-diphenylarsinophenyl*)*arsine Complexes.*—*The dichloro-osmium complex*, [$OsCl_2$(QAS)], was prepared like its phosphorus analogue. The ligand (Ia) (0·5 g.) and the substance [$OsCl_3(NO)$] (0·16 g.) in tetrahydrofurfuryl alcohol (20 c.c.) gave 0·09 g. of pure *complex* (Found: Os, 15·05; As, 23·7. $C_{54}H_{42}As_4Cl_2Os$ requires Os, 15·2; As, 23·95%).

The dichloro-palladium dichloride complex, [$PdCl_2$(QAS)]Cl_2. The chloride [PdCl(QAS)]Cl [3] (0·09 g.) in dichloromethane (25 c.c.) was treated with a 0·025M-solution of chlorine in carbon tetrachloride (17 c.c.). The orange-red solution became yellow overnight and on evaporation gave the *product* (0·08 g.) which was precipitated from dichloromethane solution by light petroleum (Found: Pd, 8·4; As, 24·1. $C_{54}H_{42}As_4Cl_4Pd$ requires Pd, 8·6; As, 24·2%).

The dichloro-platinum dichloride complex, [$PtCl_2$(QAS)]Cl_2, was prepared and purified as was its palladium analogue, the platinum(II) complex (0·1 g.) and 0·025M-chlorine (7·5 c.c.) being used (Found: Pt, 14·5; As, 22·3. $C_{54}H_{42}As_4Cl_4Pt$ requires Pt, 14·7; As, 22·6%).

Analyses.—Palladium,[3] platinum,[1] ruthenium,[2] osmium,[12] phosphorus,[13] and arsenic [3] were determined spectrophotometrically. "Ashing" of the samples for the phosphorus determinations was carried out as follows: the solid complex (*ca.* 10 mg.) was heated at 190° with a 1 : 1 mixture (2 c.c.) of 98% sulphuric acid and 73% perchloric acid for 12 hr. During this time concentrated nitric acid (1 c.c.) was added dropwise. This solution was diluted to 1 l. with water, and a sample (usually 25 c.c.) used for the determination. The osmium complexes were decomposed with a saturated solution of chromium trioxide and concentrated sulphuric acid, since the mixture of concentrated nitric and sulphuric acid recommended by Sandell [12] gave low results.

Conductivity Measurements.—These were done as described elsewhere.[2] The concentration-dependences of nitrobenzene solutions at 19° were:

Molarity	3×10^{-3}	2×10^{-3}	1×10^{-3}	5×10^{-4}	1×10^{-4}
[$PdBr_2$(TAS)], X	6·70	8·24	11·64	15·45	25·04
[PdI_2(TAS)], X	6·73	8·15	10·98	14·36	24·30

Magnetic-susceptibility Measurements.—These were done as described elsewhere.[2] Measurements over the temperature range 140—350°K showed that the previously reported weak paramagnetic susceptibility of the complex [$Ru(CNS)_2$(QAS)] is temperature-independent.

[12] Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publ., Inc., New York, 1959, p. 704.

[13] Bartlett, *J. Biol. Chem.*, 1959, **234**, 466.

Infrared Spectra.—These were recorded for Nujol or hexachlorobutadiene mulls on a Perkin-Elmer 221 spectrophotometer.

Visible and Ultraviolet Spectra.—These were recorded on a Unicam S.P. 700 spectrophotometer. The reflection spectra were recorded on an S.P. 500 spectrophotometer fitted with diffuse reflection attachment S.P. 540.

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